



## Analysis of solid solutions stability in scheelite-type molybdates and tungstates

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### ABSTRACT

Mutual solubility of bivalent metal molybdates and tungstates with scheelite structure was theoretically estimated by calculating formation enthalpies and the maximal decomposition temperatures of solid solutions at different temperatures. The theoretical stability of continuous solid solutions in binary systems of bivalent metal molybdates and tungstates was found to be higher than reported literature data. After cooling down continuous substitution solid solution should remain in following systems:  $\text{CaMoO}_4\text{--CdMoO}_4$ ,  $\text{SrMoO}_4\text{--MMoO}_4$  ( $M = \text{Ba, Pb}$ ),  $\text{BaMoO}_4\text{--PbMoO}_4$ ,  $\text{SrWO}_4\text{--MWO}_4$  ( $M = \text{Ca, Pb}$ ), and  $\text{BaWO}_4\text{--PbWO}_4$ . There is a probability that at room temperature in systems  $\text{CaMoO}_4\text{--SrMoO}_4$ ,  $\text{CaWO}_4\text{--PbWO}_4$ , and  $\text{BaWO}_4\text{--SrWO}_4$  the single homogeneity region may decompose to limited solid solutions. It was shown experimentally that a continuous series of scheelite-structure solid solutions  $M_{1-x}M_x^II\text{TO}_4$  can be formed via citrate synthesis at temperatures below 500 °C.

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### 1. Introduction

Molybdates and tungstates of the composition  $M\text{TO}_4$ , where  $M = \text{Ca, Sr, Ba, Pb, or Cd}$ ;  $T = \text{Mo or W}$ , with scheelite structure have been extensively studied as materials for X-ray and photoluminescence, low-temperature radiation detectors, solid-state lasers, catalysts, etc. [1–12]. Useful properties of such materials can be varied using binary solid solutions  $M_{1-x}M_x^II\text{TO}_4$ , where  $M, M^I = \text{Ca, Sr, Ba, Pb, or Cd}$ ;  $T = \text{Mo or W}$ , as a matrix [13–16]. For example, it was found that photoluminescence intensity of mixed tungstate  $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{WO}_4$  is higher than for individual tungstates [15].

When growing and exploiting oxide solid solution monocrystals, one should take into account not only the data on their homogeneity regions, but also the information about their stability upon cooling since in the process of crystallization these species can transform to mixtures of limited solid solutions. Perhaps, this may be the reason why the attempt to grow  $\text{Ca}_{1-x}\text{Pb}_x\text{MoO}_4$  monocrystals at  $0.1 < x < 0.5$  failed [16].

Investigations into binary systems of bivalent metal molybdates with scheelite structure are few in number and contradictory [15–21]. According to Demyanets et al. [17], primary solid solutions exist in the  $\text{SrMoO}_4\text{--CdMoO}_4$  system at 1000 °C at

concentrations 0–55% and 60–100 mol%  $\text{CdMoO}_4$ ; as the temperature lowers to 400 °C, the regions of their existence narrow to 0–23 and 96–100 mol%  $\text{CdMoO}_4$ . However, Zhuravlev et al. in [18] complete isomorphous miscibility of strontium and cadmium molybdates at  $T = 900$  °C was reported. In the  $\text{PbMoO}_4\text{--CdMoO}_4$  system at 1000 °C, the solubility boundaries correspond to compositions  $\text{Pb}_{0.5}\text{Cd}_{0.5}\text{MoO}_4$  and  $\text{Cd}_{0.8}\text{Pb}_{0.2}\text{MoO}_4$  [17]. Barium and cadmium molybdates exhibit even smaller reciprocal solubility, viz. 5–7 mol% at 1100 °C [17]. Possibly, owing to smaller differences in ionic radii of cations, a continuous series of substitutional solid solution (CSS) exists in the  $\text{CaMoO}_4\text{--SrMoO}_4$  system at 1100 °C [17] or at 800–820 °C [18], as well as in the  $\text{CaMoO}_4\text{--CdMoO}_4$  system at 1000 °C [17]. Substitution of unstable bivalent metal carbonate for individual molybdates allows continuous solid solutions to be obtained at lower temperatures: between barium and lead molybdates at 650 °C, barium and strontium – at 750 °C, calcium and lead, strontium and lead molybdates – at 900 °C [18,19].

The interaction of bivalent metal tungstates was studied in [14,15,17,18,20,21]. Only the  $\text{CaWO}_4\text{--BaWO}_4$  system exhibits limited solubility, 5–7 mol% at 1100 °C [17], while the rest tungstates–scheelites unrestrictedly mix at synthesis temperatures 815–970 °C. The miscibility of bivalent metal tungstates at lower temperatures has not been examined. It is known only that in the  $\text{SrWO}_4\text{--BaWO}_4$  system a continuous series of solid solutions remains upon cooling to 400 °C [17]. According to Chang, [21], in  $\text{CaWO}_4\text{--Sr(Pb)WO}_4$  systems, the biphasic region begins to form below 815–825 °C resulting in narrowing of primary solid

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solution concentration intervals to 5–10 mol% at 600 °C. However, a continuous series of solid solutions in the  $\text{CaWO}_4\text{--SrWO}_4$  system was obtained by Pôrto et al. in [15] by soft synthesis methods at 400–700 °C. These results show that with an increase in the reaction mixture components' activity the temperature, at which unlimited solubility in a binary system is registered, falls. The equilibrium typical of the maximal synthesis temperatures usually remains during fast cooling of samples. To derive data on real stability boundaries of solid solutions, they should be synthesized and annealed at as low temperatures as possible, e.g. using synthesis methods based on gelatinization of liquid precursors and their subsequent drying and annealing. In this study, we used for this purpose a citrate method allowing bivalent metal molybdates to be synthesized at temperatures not higher than 500 °C [22,23].

## 2. Calculation

The quantitative theory of isomorphous substitutions [24,25] makes it possible to determine reciprocal miscibility boundaries for two compounds by calculating the enthalpy of solid solution formation or enthalpy of mixing  $\Delta H_{\text{mix}}$ :

$$\Delta H_{\text{mix}} = A(\Delta D/D)^2 + B(\Delta \varepsilon)^2/2D + X_2\Delta H_{\text{I-II}}, \quad \text{cal/mol} \quad (1)$$

where  $\Delta D/D$  is the relative cation–anion distance difference,  $\Delta \varepsilon$  is the difference in cation–anion bond ionicity,  $\Delta H_{\text{I-II}}$  is the enthalpy of transition of an impurity compound to the matrix compound structure if they are not isostructural. Coefficients  $A$  and  $B$  depend on the structure and composition of the compound:

$$A = X_1X_2CmnZ_MZ_A \quad (2)$$

$$B = 332mX_1X_2Z_MZ_A\alpha \quad (3)$$

where  $C$  is the individual constant for a group of isostructural compounds [24];  $m=2$  for binary compound  $MA$ ;  $Z_M$  and  $Z_A$  are the formal degrees of oxidation of cation ( $M$ ) and anion ( $A$ );  $n$  is the coordination number in substitution position;  $\alpha$  is the reduced Madelung constant; and  $X_1$  and  $X_2$  are mole fractions of interacting compounds.

The above equations of V.S. Urusov's energy theory for isomorphous miscibility [24] were deduced using the ionic model for isoivalent substitutions in alkaline halogenides. However, complex oxides contain more than two different oxygen coordination polyhedrons  $MO_n$ , in which cation substitution is realized. Therefore, in this case, an analog of the binary compound  $MA$  in basic equations 1–3 is the coordination polyhedron  $MO_n$  [26]. In the scheelite crystal structure in  $MO_8$  polyhedron, four interatomic distances  $D(M\text{--}O)$  are smaller than the other four, that is why we used their average value  $D_{\text{av}}(M\text{--}O)$  [27–33] for analysis. In this “polyhedral substitution model”, the coefficient  $C$  characterizes coordination polyhedrons rather than the type of compound and is related with the ionicity of  $M\text{--}O$  bond by the equation [26]:

$$C = f(\varepsilon_{\text{cryst}}) = 22,800\varepsilon^2 + 10,700\varepsilon + 6130, \quad \text{cal/mol} \quad (4)$$

With substitutions in  $MO_8$  polyhedrons, for cadmium molybdate (scheelite structure)  $C=25,090$  cal/mol, while for the rest  $MTO_4$ , where  $M=\text{Ca, Sr, Ba, or Pb}$ ;  $T=\text{Mo or W}$ ,  $C=27,430$  cal/mol. Calculating the miscibility in  $MMoO_4\text{--}CdMoO_4$  systems, we used the arithmetic average of the coefficient  $C=26,260$  cal/mol. The ionicity  $\varepsilon$  of  $M\text{--}O$  bonds necessary for the calculations was computed from the electronegativities of elements [34–36]. They are given in work V. Zhuravlev [36] for different types of oxygen polyhedrons:  $\varepsilon(T\text{--}O_4)=0.35$ ,  $T=\text{Mo, W}$ ;  $\varepsilon(M\text{--}O_8)=0.76$ ,  $M=\text{Ca, Sr, Ba, Pb}$ ;  $\varepsilon(\text{Cd}\text{--}O_8)=0.72$ .

In the scheelite crystal lattice there exist two types of oxygen polyhedrons:  $MO_8$  and  $TO_4$ . Therefore, for substitutions in the cationic sublattice  $n=8$ , while for substitutions in the anionic sublattice  $n=4$ . In this study we consider substitutions only in the cationic sublattice. Oxygen polyhedrons  $MO_8$  consist of two types of ions:  $M^{2+}$  and  $O^{2-}$ , that is,  $m=2$ . Instead of formal oxidation degrees of ions  $Z_M=2$  and  $Z_O=2$ , in the polyhedral substitution model we used their effective charges  $Z_M^* = Z_M\varepsilon(M\text{--}O)$  and  $Z_O^* = Z_O\{(2\varepsilon(M\text{--}O) + \varepsilon(TO_4))/3\}$ . Since the examined compounds are isostructural,  $\Delta H_{\text{I-II}}=0$ .

In order to transfer from  $\Delta H_{\text{mix}}$  to estimation of concentration boundaries of solubility at different temperatures, the free energy of mixing of disorder solid solutions as function of composition and temperature can be given as follows [24,25]:

$$\Delta F_{\text{mix}}(x, T) = \Delta H_{\text{mix}} - T(\Delta S_{\text{conf}} + \Delta S_{\text{vib}}) \\ = x_1x_2Q(1 - T/\tau) - RT(x_1 \ln x_1 + x_2 \ln x_2) \quad (5)$$

where  $Q$  is the energy of mixing,  $\Delta S_{\text{conf}}$  and  $\Delta S_{\text{vib}}$  is the configurational and vibrational entropy,  $\tau$  is the empirical parameter equals  $2800 \pm 500$  K [25] and  $R$  is the gas constant. The critical conditions of decomposition defining the spinodal and bimodal curves are

$$\partial^2 \Delta F_{\text{mix}} / \partial x^2 = 0 \quad \text{and} \quad \partial^3 \Delta F_{\text{mix}} / \partial x^3 = 0 \quad (6a, b)$$

For “simple mixture”  $Q$  is the const., upon differentiating Eq. (1) with respect to  $x$  one obtains:

$$Q(1 - T/\tau) = RT/x_1x_2 \quad (7)$$

$$0 = RT(2x_1 - 1)x_1^2x_2^2 \quad (8)$$

For  $x=0.5$ , which on substitution into Eq. (3), yields the maximal decomposition temperatures of solid solutions  $T_{\text{max}}$ :

$$Q(1 - T/\tau) = 2RT_{\text{max}} \quad (9)$$

or

$$T_{\text{max}} = Q/[2R + (Q/\tau)] \quad (10)$$

When  $Q$  is independent of composition and does not account the vibrational entropy:

$$T_{\text{max}} = Q/2R \quad (11)$$

In phenomenological theory solid solutions  $\Delta H_{\text{mix}} = x_1x_2Q$  cal/mol [24,25] therefore

$$T_{\text{max}} = \Delta H_{\text{mix}}/4x_1x_2 \quad (12)$$

After substitution of constant terms, Eq. (12) for the systems  $MTO_4\text{--}M^I TO_4$ , where  $M, M^I = \text{Ca, Sr, Ba, or Pb}$ ;  $T = \text{Mo or W}$ ,  $\Delta \varepsilon = 0$ , is transformed as follows:

$$T_{\text{max}} = 208,470(\Delta D/D_{\text{min}})^2, \quad \text{K} \quad (13)$$

For the systems  $\text{CdTO}_4\text{--}MTO_4$ , where  $M = \text{Ca, Sr, Ba, or Pb}$ ,  $\Delta \varepsilon = 0.04$ , the maximal decomposition temperature for them was estimated from

$$T_{\text{max}} = 191,610(\Delta D/D_{\text{min}})^2 + 168 \text{K} \quad (14)$$

Knowing the maximal decomposition temperature for solid solutions, we can estimate, by means of nomograms, the variation in isomorphous miscibility limits as a function of temperature [24].

## 3. Experimental

Chemically pure barium, calcium, strontium, and cadmium nitrates and ammonium molybdate, as well as a dissolvent and chelating agent – citric acid with 5–10 cm<sup>3</sup> nitric acid added to 100 cm<sup>3</sup> solution – were used as initial reagents for synthesis. Ammonium molybdate was dissolved in an aqueous solution of citric acid in mole fraction 1:3; then metal nitrates were added to

the solution. The resulting citrate solution was slowly evaporated to dryness while mixing. During heating, a stable gel was formed preventing fractional precipitation of molybdates. This effect is unfavorable for solid solutions' synthesis, since early crystallization of  $M\text{MoO}_4$  phases increases the initial temperature of solid solution formation.

The obtained xerogels were several times re-burdened and annealed at 500 °C for 60–80 h. If, according to X-ray diffraction analysis, the samples remained in non-equilibrium, the annealing temperature was enhanced to 600–700 °C and the total time of annealing to 150–160 h. In a number of cases, the powders were pelletized; upon exposure at maximal temperatures they were ground and subjected to stabilizing annealing at 500–600 °C for 100–120 h. Such heat treatment allowed us to detect possible decomposition of the solid solutions during temperature decrease.

The single-phase constitution, equilibrium, and unit cell parameters of the samples were determined with automated diffractometers Guinier G670 and Shimadzu XRD-700 (in  $\text{CuK}\alpha$  radiation). The thermal properties of the samples were examined on a Q-1500D derivatograph (Paulic–Paulic Erdey) in platinum crucibles at heating rate 10 °C/min using 0.5–0.7 g samples.

#### 4. Results and discussion

In this experiment we found that in most of the binary molybdate systems continuous series of solid solutions (CSS) were obtained at temperatures 500–650 °C (Fig. 1) except  $\text{SrMoO}_4$ – $\text{CdMoO}_4$  and  $\text{PbMoO}_4$ – $\text{CdMoO}_4$  systems, in which limited solid solutions were formed at those temperatures, and the system  $\text{CaMoO}_4$ – $\text{BaMoO}_4$  with no solubility at 500 °C. Note that a CSS was formed in the  $\text{CaMoO}_4$ – $\text{PbMoO}_4$  system only after the synthesis

temperature had been increased to 850–900 °C, and it retained upon annealing at 500 °C for 70 h.

Spontaneous furnace cooling of the samples to room temperature prevents exact determination of the temperature, at which the equilibrium state is formed during cooling; therefore, in Fig. 1 we indicated synthesis or stabilizing annealing temperatures.

With the use of citrate precursors we found that most of the solid solutions in the examined molybdate systems with scheelite structure are more stable than was suggested in the previous studies [17–20], where individual molybdates  $\text{MTO}_4$  [17] or bivalent metal carbonates and lead and molybdenum oxides [18,19] were used for solid-phase synthesis. Even replacement of individual molybdates by bivalent metal oxides and impermanent carbonates or ammonium molybdate provides a reduction in the CSS synthesis temperature by 200–300 °C, whereas nitrate–citrate precursors lower the temperature range for mixed molybdate synthesis to 500–600 °C. Undoubtedly, progress in soft synthesis methods will enable one to decrease the upper temperature of this range and to determine more accurately the boundaries of CSS existence at 20–500 °C. Meanwhile, the problem of relatively low temperature stability of CSS was tackled by the authors on the basis of theoretical analysis of reciprocal solubility.

The crystal lattice parameters of the examined solid solutions change linearly with the composition (Fig. 1); therefore they can be considered as regular solutions to be used in the calculation of Eqs. (6) and (7) [24]. Necessary data on  $M$ –O distances were taken from [27–33] (Table 1).

Analysis of  $T_{\text{max}}$  (Table 2) shows that upon cooling to room temperatures CSS should remain in  $\text{CaMoO}_4$ – $\text{CdMoO}_4$ ,  $\text{SrMoO}_4$ – $\text{MMoO}_4$  ( $M = \text{Ba}, \text{Pb}$ ),  $\text{BaMoO}_4$ – $\text{PbMoO}_4$ ,  $\text{CaWO}_4$ – $\text{SrWO}_4$ ,  $\text{SrWO}_4$ – $\text{PbWO}_4$ , and  $\text{BaWO}_4$ – $\text{PbWO}_4$  systems. CSS in  $\text{CaMoO}_4$ – $\text{SrMoO}_4$ ,  $\text{CaWO}_4$ – $\text{PbWO}_4$ , and  $\text{BaWO}_4$ – $\text{SrWO}_4$  systems are less stable; here there is a probability that on long storage at room temperatures the single homogeneity region may decompose to limited solid solutions since their  $T_{\text{max}}$  values are within the 440–585 K range.

Miscibility calculations for the rest systems confirm the existence of limited solid solutions of different extent below 500 °C. For example, the state diagram for the  $\text{PbMoO}_4$ – $\text{CdMoO}_4$  system plotted on the basis of DTA results (Fig. 2) shows that reciprocal solubility of initial compounds is maximal at the eutectic temperature  $1000 \pm 5$  °C reaching ~30 mol%  $\text{CdMoO}_4$  and ~20 mol%  $\text{PbMoO}_4$  and decreases with temperature: at 450–500 °C the limiting compositions of the solid solutions contain ~15 mol%  $\text{CdMoO}_4$  and ~5 mol%  $\text{PbMoO}_4$ . The calculated solubility boundaries are rather close to the experimental values: 35 mol%  $\text{CdMoO}_4$  and 24 mol%  $\text{PbMoO}_4$  at 995 °C and ~8 mol%  $\text{CdMoO}_4$  and < 5 mol%  $\text{PbMoO}_4$  at 500 °C.

It was established experimentally that in the  $\text{PbMoO}_4$ – $\text{CaMoO}_4$  system at 500 °C there are limited primary solid solutions in the

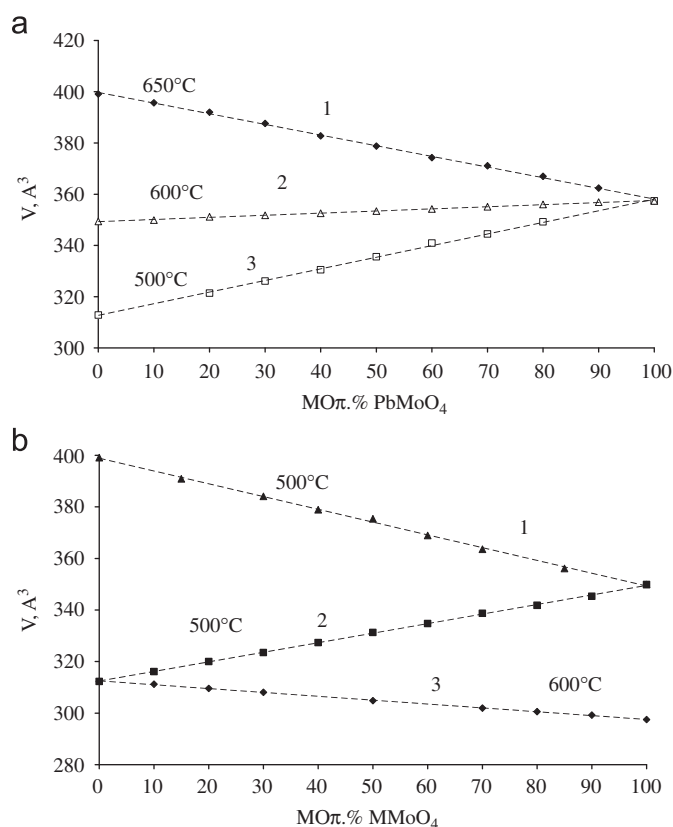


Fig. 1. Variation in the unit cell volume for solid solutions of bivalent metal molybdates: (a)  $\text{BaMoO}_4$ – $\text{PbMoO}_4$  (1),  $\text{SrMoO}_4$ – $\text{PbMoO}_4$  (2),  $\text{CaMoO}_4$ – $\text{PbMoO}_4$  (3) and (b)  $\text{BaMoO}_4$ – $\text{SrMoO}_4$  (1),  $\text{CaMoO}_4$ – $\text{SrMoO}_4$  (2),  $\text{CaMoO}_4$ – $\text{CdMoO}_4$  (3).

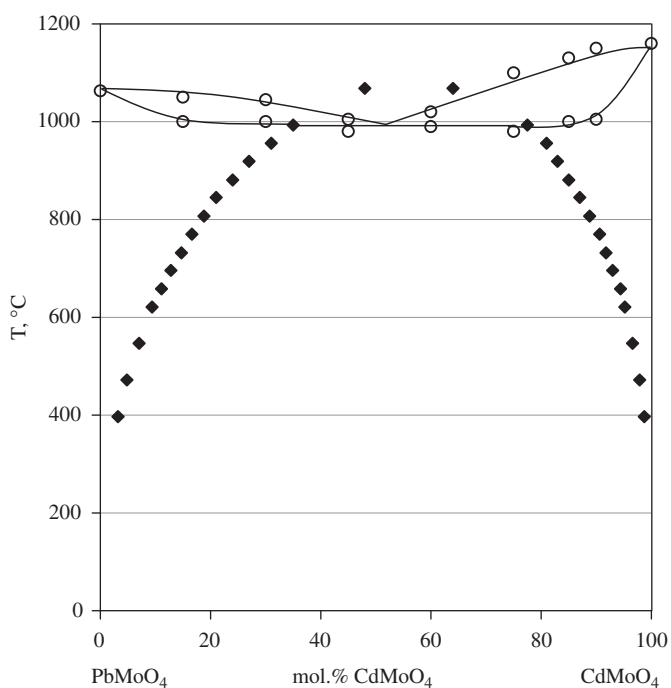
Table 1  
Crystal cell parameters and distances in oxygen polyhedrons of molybdates and tungstates with scheelite structure.

Composition	$a$ (Å)	$c$ (Å)	$D(M-O)_{av}$ (Å)	$D(T-O)_{av}$ (Å)	$\varepsilon(M-O)$	References
$\text{CaMoO}_4$	5.226	11.430	2.466	1.757	0.76	[33]
$\text{SrMoO}_4$	5.394	12.020	2.597	1.767	0.76	[27]
$\text{BaMoO}_4$	5.62	12.82	2.688	1.765	0.76	[27,31]
$\text{PbMoO}_4$	5.4340	12.107	2.624	1.769	0.76	[33]
$\text{CdMoO}_4$	5.155	11.194	2.427	1.730	0.72	[32]
$\text{CaWO}_4$	5.243	11.376	2.46	1.78	0.76	[28,29]
$\text{SrWO}_4$	5.417	11.951	2.556	1.853	0.76	[33]
$\text{PbWO}_4$	5.462	12.048	2.578	1.868	0.76	[33]
$\text{BaWO}_4$	5.612	12.706	2.675	1.935	0.76	[33]

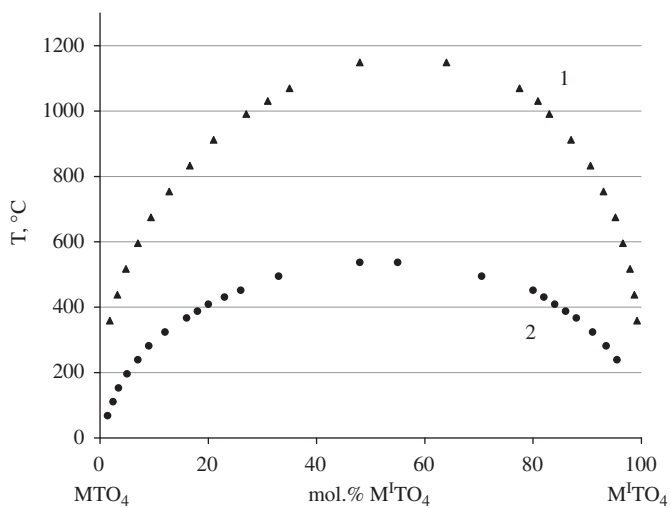
**Table 2**

Maximal theoretical decomposition temperatures of solid solutions in  $MTO_4$ – $M^1TO_4$  systems, where  $M, M^1 = Ca, Sr, Ba, Pb, Cd$ ;  $T = Mo, W$ .

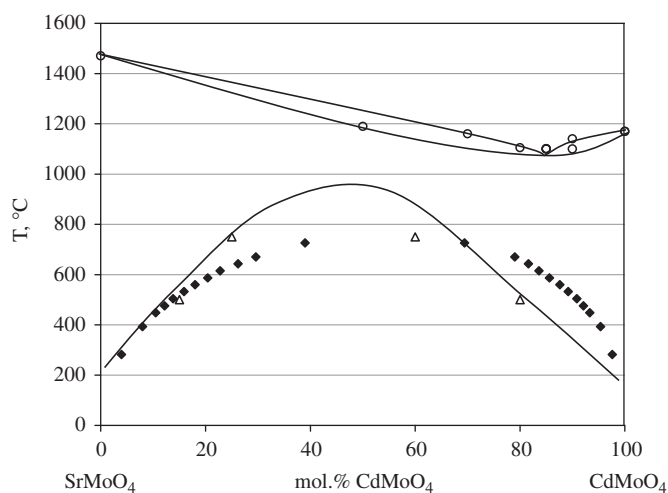
$MTO_4$ – $M^1TO_4$	$\Delta D/D_{\min}$ (%)	$T_{\max}$ (K)	$MTO_4$ – $M^1TO_4$	$\Delta D/D_{\min}$ (%)	$T_{\max}$ , K
<i>Molybdates</i>					
CaMoO <sub>4</sub> –SrMoO <sub>4</sub>	5.3	585	SrMoO <sub>4</sub> –PbMoO <sub>4</sub>	1.0	20
CaMoO <sub>4</sub> –BaMoO <sub>4</sub>	9.0	1690	SrMoO <sub>4</sub> –CdMoO <sub>4</sub>	7.0	1110
CaMoO <sub>4</sub> –PbMoO <sub>4</sub>	6.4	853	BaMoO <sub>4</sub> –PbMoO <sub>4</sub>	2.4	120
CaMoO <sub>4</sub> –CdMoO <sub>4</sub>	1.6	220	BaMoO <sub>4</sub> –CdMoO <sub>4</sub>	10.8	2400
SrMoO <sub>4</sub> –BaMoO <sub>4</sub>	3.5	255	PbMoO <sub>4</sub> –CdMoO <sub>4</sub>	8.3	1490
<i>Tungstates</i>					
CaWO <sub>4</sub> –SrWO <sub>4</sub>	3.9	320	SrWO <sub>4</sub> –PbWO <sub>4</sub>	0.8	15
CaWO <sub>4</sub> –BaWO <sub>4</sub>	8.7	1580	SrWO <sub>4</sub> –BaWO <sub>4</sub>	4.6	440
CaWO <sub>4</sub> –PbWO <sub>4</sub>	4.8	480	BaWO <sub>4</sub> –PbWO <sub>4</sub>	3.8	300



**Fig. 2.** State diagram of the  $PbMoO_4$ – $CdMoO_4$  system.  $\circ$ —DTA dates;  $\blacklozenge$ —calculated boundaries of solid solutions.



**Fig. 3.** Calculated boundaries of solid solutions in  $BaWO_4$ – $CaWO_4$  (1) and  $PbMoO_4$ – $CaMoO_4$  (2) systems.

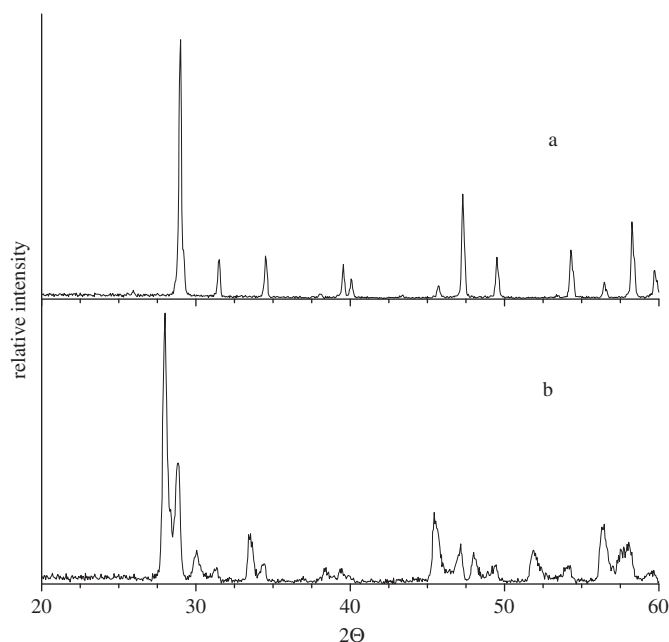


**Fig. 4.** State diagram of the  $SrMoO_4$ – $CdMoO_4$  system.  $\circ$ —DTA dates;  $\blacklozenge$ —calculated boundaries of solid solutions;  $\blacktriangle$ —experimental boundaries of solid solutions.

concentration regions 0–30 and 80–100 mol%  $CaMoO_4$ . These data are in good agreement with the theoretical solubility boundaries: 0–33 and 71–100 mol%  $CaMoO_4$  (Fig. 3). Our inference about CSS decomposition below 580 °C is supported by the detected two-phase constitution of the  $Pb_{0.5}Ca_{0.5}MoO_4$  sample upon its crystallization from the melt [16].

The results of thermal analysis of  $SrMoO_4$ – $CdMoO_4$  samples (Fig. 4) are indicative of a eutectic transformation of CSS at  $1100 \pm 5$  °C in the region of 85 mol%  $CdMoO_4$ , confirming the conclusion about complete reciprocal miscibility of cadmium and strontium molybdates above 1000 °C. With a decrease in temperature, CSS decompose: at synthesis temperature 500 °C there are two regions of primary solid solutions with the range ~15–20 mol% corresponding approximately to the solubility limits reported in [17] for 400 °C: 23 mol%  $CdMoO_4$  and 4 mol%  $SrMoO_4$ . The theoretical solubility of strontium molybdate in cadmium molybdate is smaller than the experimental value and amounts to 9 mol% at 500 °C, whereas reciprocal solubility, 13.8 mol%  $CdMoO_4$ , is close to the experimental data. The solid solution decomposition dome in the  $SrMoO_4$ – $CdMoO_4$  system (Fig. 4) plotted on the basis of our data taken from Zhuravlev et al. [18] is asymmetrically displaced towards strontium molybdate showing greater isomorphic capacitance of cadmium–oxygen bonds. This is likely to be due to higher covalency of cadmium–oxygen bonds. Theoretically, reasoning from smaller sizes of substitution polyhedrons, the  $CdMoO_4$  matrix should have smaller substitution capacitance [24]. All cadmium–molybdate free systems obey the Goldschmidt–Fersman isomorphic substitution





**Fig. 5.** X-ray diffraction patterns of (a)  $\text{CaMoO}_4$  sample after 15 h annealing and (b)  $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{MoO}_4$  sample after 60 h annealing at 500 °C.

polarity rule [24], when ions with smaller radii enter into the common crystal structure more readily than ions with larger radii.

The maximal relative differences in interatomic distances in coordination polyhedrons  $\text{MO}_8$  are typical of the  $\text{BaMoO}_4$ – $\text{CdMoO}_4$  ( $\Delta D/D_{\min} = 10.8\%$ ) and  $\text{BaMoO}_4$ – $\text{CaMoO}_4$  systems ( $\Delta D/D_{\min} = 9.0\%$ ); their  $T_{\max}$  values are, respectively, 2400 K and 1690 K suggesting practical insolubility of compounds below 1000 °C.

It is known [17,18,20,21] that CSS exist in all binary tungstate–scheelite systems except  $\text{BaWO}_4$ – $\text{CaWO}_4$ . From calculations, in this system, CSS can form only at temperatures above 1200–1300 °C (Fig. 3). Theoretical solubility in the  $\text{BaWO}_4$ – $\text{CaWO}_4$  system at 1000 °C is 27 mol%  $\text{CaWO}_4$  and 17 mol%  $\text{BaWO}_4$ , which is appreciably higher than that found by Chang [21]: 4.5 mol%  $\text{CaWO}_4$  and 2.5 mol%  $\text{BaWO}_4$ . The calculations show (Table 2) that tungstate CSS will be stable at room temperatures. This is also true for the  $\text{SrWO}_4$ – $\text{CaWO}_4$  system, for which Chang [21] could not obtain any CSS below 825 °C. We believe that the solid solution decomposition temperatures in [21] were over-estimated since the initial components were individual bivalent metal tungstates and molybdates, the interaction between which below 600 °C, limited by the rate of initial phase's diffusion through a solid solution layer, is very slow. Our experiments showed that annealing of a mixture of calcium and strontium tungstates at 600 °C for 150 h does not lead to the formation of single-phase samples  $\text{Sr}_{1-x}\text{Ca}_x\text{WO}_4$  with  $x = 0.4$ – $0.6$ . Besides enhanced temperature, additional grinding and pelletizing are required for synthesis of single-phase solid solution samples.

Note that the time of solid phase synthesis of single-phase solid solutions ( $x = 0.4$ – $0.6$ ) is much greater than the time for individual initial compounds synthesis. For example, a calcium molybdate sample becomes a single-phase compound upon 15 h annealing at 500 °C (Fig. 5), whereas a  $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{MoO}_4$  sample even after 60 h thermal treatment at the same temperature consists of a mixture of two solid solutions with approximate compositions  $\text{Ca}_{0.8}\text{Sr}_{0.2}\text{MoO}_4$  and  $\text{Ca}_{0.2}\text{Sr}_{0.8}\text{MoO}_4$ .

The observed discrepancies in the theoretical and experimental estimations of solubility boundaries may be due to (1) the

misfit between the model of regular solutions and the actual situation and (2) delayed formation (decomposition) of oxide solid solutions below 700–800 °C. The error in homogeneity boundaries and CSS decomposition temperature calculation does not exceed  $\pm(5$ – $10)$  mol% and  $\pm 100$  °C, respectively.

## 5. Conclusion

Comparison of experiments and theoretical calculations of reciprocal solubility of bivalent metal molybdates and tungstates with scheelite structure allows us to conclude that the chosen model of oxide compounds can be used for a priori analysis of the interaction between pairs of complex oxides with heterodesmic crystal structures. The calculations performed reveal that most of the examined binary systems contain continuous series of solid solutions stable at room temperatures.

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